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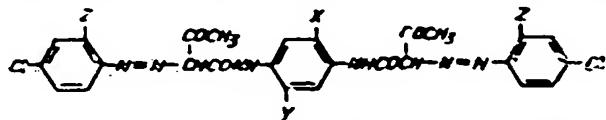
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(54) NEW DISAZO PIGMENTS, PROCESSES FOR THEIR MANUFACTURE AND USE

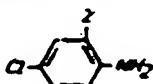
(71) We, CIBA-GEIGY AG, a Swiss body corporate, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides, as new compounds, the disazo pigments of the formula:

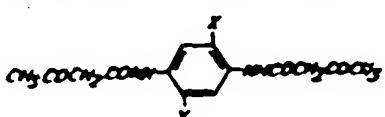


wherein Z represents halogen, methyl, nitro, cyano, trifluoromethyl, or alkoxy of 1 to 4 carbon atoms, X represents hydrogen, halogen, an alkyl or alkoxy group of 1 to 4 carbon atoms, nitro, cyano or trifluoromethyl and Y represents hydrogen, halogen, alkyl of 1 to 4 carbon atoms or trifluoromethyl, and when Z represents methyl or alkoxy only one of X and Y may be halogen.

According to a feature of the invention, these pigments are obtained by coupling a diazo or diazocomino compound of an amine of the formula:

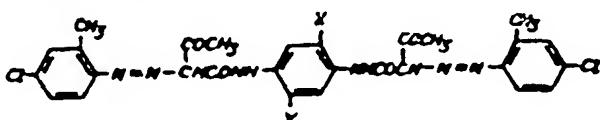


with a bis-acetoacetyl-*p*-phenylenediamine of the formula



in the molar ratio of 2:1.

Diazo pigments of the formula



wherein X and Y denote hydrogen or X denotes methyl and Y denotes chlorine, are of particular interest.

As examples of diazo components there may be mentioned the diazo compounds derived from 2-methyl-4-chloroaniline, 2-methoxy-4-chloroaniline, 2-nitro-4-chloroaniline, 2-cyano-4-chloroaniline, 2,4-dichloroaniline and 2-trifluoromethyl-4-chloroaniline.

The coupling components are obtained in a simple manner by the action of diisopropene or ethyl acetoacetate on the appropriate phenylenediamines such as, in particular, 1,4-phenylenediamine and also 2-methyl-1,4-phenylenediamine, 2-methoxy-1,4-phenylenediamine, 2-ethoxy-1,4-phenylenediamine, 2-propoxy-1,4-phenylenediamine, 2-isoproxy-1,4-phenylenediamine, 2-butoxy-1,4-phenylenediamine, 2-nitro-1,4-

phenylenediamine, 2-cyano-1,4-phenylenediamine, 2-trifluoromethyl-1,4-phenylenediamine, 2,5-dimethyl-1,4-phenylenediamine, 2,5-bis-trifluoromethyl-1,4-phenylenediamine, 2-chloro-5-methyl-1,4-phenylenediamine, 2-methyl-5-methoxy-1,4-phenylenediamine and 2-methyl-5-ethoxy-1,4-phenylenediamine.

The coupling preferably takes place in a weakly acid medium, appropriately in the presence of customary agents which promote coupling. Examples of such agents are dispersing agents, for example aralkylsulphonates, such as dodecylbenzenesulphonate, or 1,1'-dinaphthylmethane-2,2'-disulphonic acid or polycondensation products of alkylene oxides. The dispersion of the coupling component can also advantageously contain protective colloids, for example methylcellulose, or minor amounts of inert organic solvents which are sparingly soluble or insoluble in water, for example optionally halogenated or nitrated aromatic hydrocarbons, such as benzene, toluene, xylene, chlorobenzene, dichlorobenzene or nitrobenzene, as well as aliphatic halogenated hydrocarbons, such as, for example, carbon tetrachloride or trichloroethylene, and also water-miscible organic solvents, such as acetone, methyl ethyl ketone, methanol, ethanol or isopropanol.

The coupling can also be carried out advantageously by continuously combining an acid solution of the diazonium salt with an alkaline solution of the coupling component in a mixing nozzle, whereupon immediate coupling of the components occurs. Care must be taken that the diazo components and coupling components are present in equimolecular amounts in the mixing nozzle and it has proved advantageous to use a slight excess of the diazo component. This is most simply effected by monitoring the pH value of the liquid in the mixing nozzle. It is also necessary to ensure that the two solutions are vigorously intermixed in the mixing nozzle. The resulting dyestuff dispersion is continuously withdrawn from the mixing nozzle and the dyestuff is isolated by filtration.

The coupling can also be effected by heating a diazoamino compound of the amine to be employed as the diazo component with the diacetoxycetylphenylenediamine in an organic solvent, optionally in an aqueous-organic solvent, preferably in the presence of an acid.

The diazoamino compounds used in the process are obtained by known processes by condensing a diazonium salt of the amine serving as the diazo component with a primary, or preferably with a secondary, amine. The most diverse amines are suitable for this purpose, for example aliphatic amines, such as methylamine, ethylamine, ethanolamine, propylamine, butylamine, hexylamine and especially dimethylamine, diethylamine, diethanolamine, methyl-ether amine, dipropylamine or dibutylamine, aminoacetic acid, methylaminoacetic acid, ethylaminoacetic acid, aminochanesulphonic acid, methylaminoethanesulphonic acid, guanylethanesulphonic acid, β -aminoethylsulphuric acid, aliphatic amines such as cyclohexylamine, N-methylcyclohexylamine, dicyclohexylamine, aromatic amines such as 4-aminobenzoic acid, sulphamic acid, 4-sulpho-2-aminobenzoic acid, (4-sulphophenyl)-guanidine, 4-N-methyl-aminobenzoic acid, 4-ethylaminobenzoic acid, 1-aminonaphthalene-sulphonic acid, 1-aminonaphthalene-2,4-disulphonic acid, heterocyclic amines such as piperidine, morpholine, pyrrolidine, and dihydroindole and finally also sodium cyanamide or dicyandiamide.

As a rule, the diazoamino compounds obtained are sparingly soluble in cold water and can, if necessary after washing out, be isolated in a crystalline form from the reaction medium. In many cases, the moist press cakes can be used for the further reaction. In isolated cases it may prove advisable to dehydrate the diazoamino compounds prior to the reaction by vacuum drying or, after suspending the moist press cake in a solvent, to remove the water by azeotropic distillation.

The coupling of the diazoamino compound with the bis-acetoxycetyl-p-phenylenediamine is carried out in an organic solvent, for example chlorobenzene, o-dichlorobenzene, nitrobenzene, pyridine, ethylene glycol, ethylene glycol monomethyl ether or monoethyl ether, dimethylformamide, N-methylpyrrolidone, formic acid or acetic acid. When using solvents which are miscible with water it is not necessary to use the diazoamino compound in an anhydrous form. For example, the water-moist filter cakes can be used. The splitting of the diazoamino compound which precedes the coupling is carried out in an acid medium. If neutral solvents are used, the addition of an acid, for example hydrogen chloride, sulphuric acid, formic acid, acetic acid or chloroacetic acid, is necessary.

The coupling can appropriately be carried out warm, preferably at temperatures of between 80 and 180°C, and in general takes place very rapidly and completely.

Because of their insolubility the pigments obtained can be isolated from the reaction mixtures by filtration. It is advantageous to subject the pigments to an after-treatment with an organic solvent which preferably boils above 100°C. Benzenes which

are substituted by halogen atoms or alkyl or nitro groups, such as xylenes, chlorobenzenes, α -dichlorobenzene or nitrobenzene, as well as pyridine bases, such as pyridine, picoline or quinoline, and also ketones, such as cyclohexanone, ethers, such as ethylene glycol monomethyl ether or monoethyl ether, amides, such as dimethylformamide or N -methylpyrrolidone, and tetrahydrothiophene dioxide, are particularly suitable for this purpose.

The after-treatment is preferably carried out by heating the pigment, in the solvent, to 100–180°C, whereupon in many cases an increase in particle size occurs, which has a favourable effect on the fastness of the resulting pigments to light and to migration.

Finally, the coupling can also be carried out by suspending the amine to be diazotized, with the coupling component, in a molar ratio of 2:1 in an organic solvent and treating the mixture with a diazotising agent, especially an ester of nitrous acid, such as methyl nitrite, ethyl nitrite, butyl nitrite, amyl nitrite or octyl nitrite.

The new pigments in a finely divided form can be used for pigmenting high molecular weight organic material, for example cellulose ethers and cellulose esters, polyamides or polyurethanes or polyesters, acetylcellulose, nitrocellulose, natural resins or synthetic resins, such as polymerisation resins or polycondensation resins, for example aminoplasts, especially urea-formaldehyde and melamine-formaldehyde resins, alkyl resins, phenoplasts, polycarbonates, polyolefines, such as polystyrene, polyvinyl chloride, polyethylene, polypropylene, polyacrylonitrile, polyacrylic acid esters, thermoplastic or thermosetting acrylic resins, rubber, casein, silicone and silicone resins, individually or as mixtures.

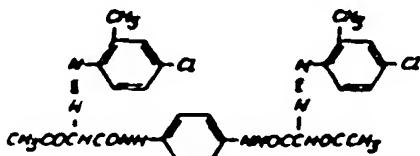
It is immaterial whether the high molecular weight compounds mentioned are in the form of plastic compositions or melts or in the form of spinning solutions, lacquers, paints or printing inks. Depending on the end use, it may be advantageous to employ the new pigments as toners or in the form of preparations. Preparations can, for example, contain, additionally to the pure pigment, natural resins, for example abietic acid or its esters, ethylcellulose, cellulose acetobutyrate, alkaline earth metal salts of higher fatty acids, fatty amines, for example stearylamine or rosin amine, vinyl chloride-vinyl acetate copolymers, polyacrylonitrile or polyterpene resins or water-soluble dyestuffs, for example dyestuff-sulphonic acids or their alkaline earth metal salts.

In the Examples which follow, the parts, unless otherwise stated, denote parts by weight and the percentages denote percentages by weight. The relationship of parts by weight to parts by volume is the same as that of the kilogram to the litre.

Example 1.

12.45 parts of 2-methyl-4-chloro-aniline in 100 parts by volume of glacial acetic acid are stirred with 25 parts by volume of concentrated hydrochloric acid, whereupon the hydrochloride of the base is formed. The mixture is then cooled to -5°C by adding 600 parts of ice and diazotisation is carried out by adding 24 parts by volume of 4 N sodium nitrite. The yellow diazo solution is stirred at 0–5°C until only traces of nitrous acid remain detectable. The diazo solution is then clarified by filtration, with addition of a little decolourising charcoal. The filtrate is brought to pH 4 by adding 48 parts of anhydrous crystalline sodium acetate.

At the same time, 11.00 parts of 1,4-bis-acetoacetylaminobenzene and 12 parts by volume of 40% strength sodium hydroxide solution are dissolved in 800 parts of water and 5 parts of n -butyl-sulphorcinolate are added. This solution is clarified by filtration with 0.5 part of decolourising charcoal and is then added dropwise over the course of 1–1½ hours to the diazo solution, whilst stirring well. In the course thereof, the temperature of the reaction mixture rises to 15–20°C. After completion of the dropwise addition diazo compound is no longer detectable in the mixture. The mixture is stirred for one hour at room temperature, then warmed to 80–85°C over the course of 1 hour and filtered hot, and the product is washed with hot water until free of salt. After drying at 95–100°C in vacuo, 22.5 parts of an orange-yellow dyestuff of the formula



are obtained.

22 parts of the pigment thus obtained are stirred in 670 parts by volume of *o*-dichlorobenzene for 3.5 hours at 180—190°C. In the course thereof, the dyestuff assumes a homogeneous crystalline form. Yellowish crystalline aggregates of 5—10 μ length are detectable under the microscope. The product is filtered off at 180°C and washed with hot *o*-dichlorobenzene until the filtrate issues colourless, the *o*-dichlorobenzene is displaced by methanol and the product is finally again washed with hot water. After drying, 18 parts of a luminous yellow pigment dyestuff are obtained. It dyes plastics such as PVC (polyvinyl chloride), in greenish-tinged yellow shades having excellent fastness to migration. The treatment in the organic solvent can also be carried out directly with the moist filter cake without prior drying. Thus it is possible to stir the moist press cake in picoline at 100—120°C, filter it and wash it with methanol and subsequently with dilute hydrochloric acid, or to stir the moist press cake in chlorobenzene, *o*-dichlorobenzene or nitrobenzene and free it of water by azeotropic distillation and then to work up the product as described above.

The table which follows describes further dyestuffs which are obtained by coupling the diazotised bases of Column I with the bis-acetoacetic acid arylides of the diamines of Column II. Column III indicates the colour shade of the PVC film coloured with 0.2% of these pigments.

TABLE I

| Example No. | Diazo base | Bis-acetoacetyl compound of the diamine | 0.2% colouration in PVC |
|-------------|-----------------------------------|--|-------------------------|
| 2 | 2-methyl-4-chloroaniline | 2-methyl-1,4-phenylenediamine | light yellow |
| 3 | 2-methyl-4-chloroaniline | 2-methoxy-1,4-phenylenediamine | yellow |
| 4 | 2-methyl-4-chloroaniline | 2-ethoxy-1,4-phenylenediamine | yellow |
| 5 | 2-methyl-4-chloroaniline | 2-propoxy-1,4-phenylenediamine | yellow |
| 6 | 2-methyl-4-chloroaniline | 2-i-propoxy-1,4-phenylenediamine | yellow |
| 7 | 2-methyl-4-chloroaniline | 2-n-butyloxy-1,4-phenylenediamine | yellow |
| 8 | 2-methyl-4-chloroaniline | 2-trichloromethoxy-1,4-phenylenediamine | yellow |
| 9 | 2-methyl-4-chloroaniline | 2-methoxy-1,4-phenylene diamine | yellow |
| 10 | 2-methyl-4-chloroaniline | 2-methyl-5-propoxy-1,4-phenylene-diamine | yellow |
| 11 | 2-methyl-4-chloroaniline | 2-methyl-5-i-propoxy-1,4-phenylene-diamine | yellow |
| 12 | 2-methyl-4-chloroaniline | 2-methyl-5-n-butoxy-1,4-phenylene-diamine | yellow |
| 13 | 2-ethyl-4-chloroaniline | 2,5-dimethyl-1,4-phenylenediamine | yellow |
| 14 | 2-methyl-4-chloroaniline | 2-chloro-5-methyl-1,4-phenylene-diamine | reddish-tinged yellow |
| 15 | 2-methyl-4-chloroaniline | 2-trifluoromethyl-1,4-phenylenediamine | greenish-tinged yellow |
| 16 | 2-methyl-4-chloroaniline | 2-cyano-1,4-phenylenediamine | greenish-tinged yellow |
| 17 | 2-methyl-4-chloroaniline | 2-nitro-1,4-phenylenediamine | greenish-tinged yellow |
| 18 | 2-trifluoromethyl-4-chloroaniline | 1,4-phenylenediamine | yellow |
| 19 | 2-trifluoromethyl-4-chloroaniline | 2-chloro-1,4-phenylenediamine | yellow |

TABLE I (Continued)

| Example No. | Diazo base | Bis-acetoxycetyl compound of the diamine | 0.2% colouration in PC |
|-------------|-----------------------------------|--|------------------------|
| 20 | 2-trifluoromethyl-4-chloroaniline | 2-bromo-1,4-phenylenediamine | yellow |
| 21 | 2-trifluoromethyl-4-chloroaniline | 2-(1-fluoromethyl)-1,4-phenylenediamine | orange-yellow |
| 22 | 2-trifluoromethyl-4-chloroaniline | 2-cyano-1,4-phenylenediamine | orange-yellow |
| 23 | 2-trifluoromethyl-4-chloroaniline | 2-nitro-1,4-phenylenediamine | orange-yellow |
| 24 | 2-trifluoromethyl-4-chloroaniline | 2-methyl-1,4-phenylenediamine | orange-yellow |
| 25 | 2-trifluoromethyl-4-chloroaniline | 2-methoxy-1,4-phenylenediamine | orange-yellow |
| 26 | 2-trifluoromethyl-4-chloroaniline | 2-ethoxy-1,4-phenylenediamine | greenish-tinged yellow |
| 27 | 2-trifluoromethyl-4-chloroaniline | 2,5-dichloro-1,4-phenylenediamine | greenish-tinged yellow |
| 28 | 2-trifluoromethyl-4-chloroaniline | 2,5-dichloro-1,4-phenylenediamine | greenish-tinged yellow |
| 29 | 2-trifluoromethyl-4-chloroaniline | 2,5-bis-trifluoromethyl-1,4-phenylenediamine | greenish-tinged yellow |
| 30 | 2-trifluoromethyl-4-chloroaniline | 2-chloro-5-ethoxy-1,4-phenylenediamine | greenish-tinged yellow |
| 31 | 2-trifluoromethyl-4-chloroaniline | 2-chloro-5-ethoxy-1,4-phenylenediamine | greenish-tinged yellow |
| 32 | 2-trifluoromethyl-4-chloroaniline | 2,5-dimethyl-1,4-phenylenediamine | greenish-tinged yellow |
| 33 | 2-trifluoromethyl-4-chloroaniline | 2-methoxy-5-methyl-1,4-phenylenediamine | yellow |
| 34 | 2-trifluoromethyl-4-chloroaniline | 2-chloro-5-methyl-1,4-phenylenediamine | yellow |
| 35 | 2-cyano-4-chloroaniline | 1,4-phenylenediamine | " |
| 36 | " | 2-chloro-1,4-phenylenediamine | " |
| 37 | " | 2-chloro-5-methoxy-1,4-phenylenediamine | greenish-tinged yellow |
| 38 | 1,4-dichloroaniline | 1,4-phenylenediamine | yellow |

TABLE I (Continued)

| Example No. | Diazo base | Bis-acetoacetyl compound of the diamine | 0.2% colouration in PVC |
|-------------|---------------------|--|-------------------------|
| 39 | 2,4-dichloroaniline | 2-chloro-5-methoxy-1,4-phenylene-diamine | yellow |
| 40 | " | 2-chloro-5-methyl-1,4-phenylene-diamine | yellow |

Example 41.

12.45 parts of 2-methyl-1,4-chloroaniline and 11 parts of 1,4-bis-acetoacetylaminobenzene are suspended in a mixture of 400 parts by volume of ethylene glycol monomethyl ether and 100 parts by volume of glacial acetic acid. Thereafter the suspension is warmed to 90—100°C and stirred until complete solution has occurred. The mixture is then stirred until it has cooled to room temperature. 60 parts by volume of nitric nitrite, as a 2 N solution in *o*-dichlorobenzene, are now slowly added to the solution obtained. This immediately produces a yellowish-tinted fine suspension and the temperature slowly rises to 38°C. After completion of the dropwise addition, the mixture is stirred for a further hour at room temperature, which ultimately produces an orange-yellow suspension. The mixture is then warmed to 80—90°C and stirred at this temperature for a further 15 hours. The pigment thus assumes a homogeneous form and fine yellow amorphous aggregates of size 5—10 μ are recognisable under the microscope.

15 Therafter the mixture is filtered at 80°C and washed with hot ethylene glycol monomethyl ether until the filtrate issues colourless. The filter residue is then rinsed with a little hot dimethylformamide and ethanol and dried in *vacuo* at 70°C.

16 parts of a yellow pigment are thus obtained.

To improve the form, this quantity of material can now be stirred with 420 parts by volume of dimethylformamide. Thereafter the mixture is warmed to 160—170°C and stirred for a further 15 hours at this temperature. This produces a fine yellow suspension and fine crystalline aggregates of size 5 μ , can be seen under the microscope.

20 The mixture is then filtered at 150°C and the product is washed with boiling dimethylformamide until the filtrate has only a pale colour. The filter residue is then rinsed with boiling ethylene glycol monomethyl ether until the filtrate is colourless. The ethylene glycol monomethyl ether is then displaced with a little ethanol and the filter residue is dried in *vacuo* at 70°C.

The yield is 12 parts, with the yellow colour of the pigment appearing somewhat more luminous than before the treatment.

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Example 42.

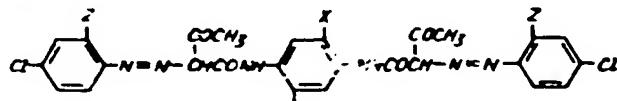
65 parts of stabilised polyvinyl chloride, 35 parts of diethyl phthalate and 0.2 part of the pigment obtained according to Example 1 are stirred together and then milled at 14°C on a two-bowl calendar for 7 minutes. A yellow-coloured film of very good fastness to light and to migration is obtained.

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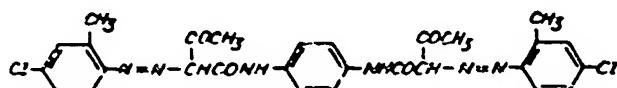
WHAT THE CLAIM IS:-

1. Disazo pigments of the formula:



5 wherein Z represents halogen, methyl, nitro, cyano, trifluoromethyl, or alkoxy of 1 to 4 carbon atoms, X represents hydrogen, halogen, an alkyl or alkoxy group of 1 to 4 carbon atoms, nitro, cyano, or trifluoromethyl and Y represents hydrogen, halogen, alkyl of 1 to 4 carbon atoms or trifluoroethyl, and when Z represents methyl or alkoxy only one of X and Y may be halogen.

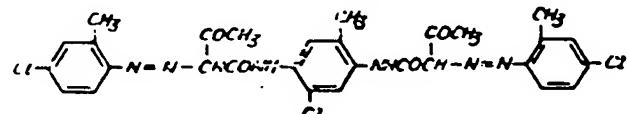
2. Disazo pigment of the formula:



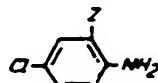
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3. Disazo pigment of the formula:



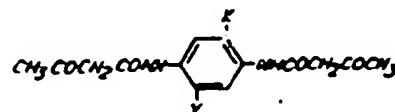
4. Process for the manufacture of disazo pigments as claimed in claim 1 which comprises coupling a diazo or diazoamino compound of an amine of the formula:



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with a bis-acetoacetyl- β -naphylenediamine of the formula:



in the molar ratio of 2:1.

5. Process according to claim 4, in which Z is methyl.

6. Process according to claim 4 or 5, in which X and Y are both hydrogen.

7. Process according to claim 4 or 5, in which X is methyl and Y is chlorine.

8. Process according to any of claims 4 to 7, in which the pigments obtained are subjected to an after-treatment with an organic solvent.

9. Process according to claim 4 substantially as described in any one of the foregoing Examples 1 to 41.

10. A pigment as claimed in claim 1 when manufactured by the process of any of claims 4 to 9.

11. A high molecular weight organic material pigmented with a pigment according to any of claims 1 to 3 or 10.

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